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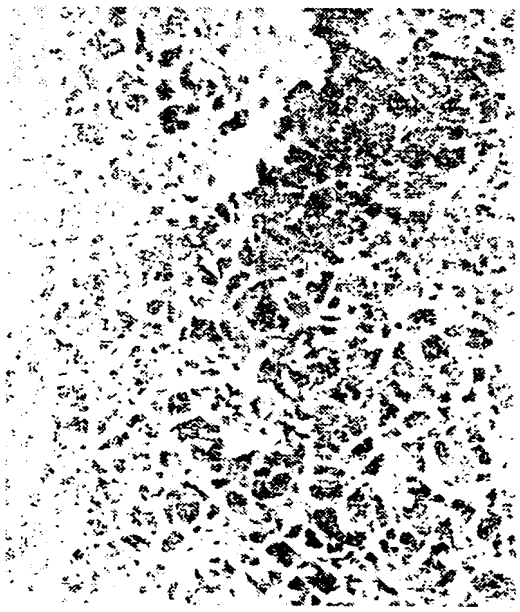

(57) Abstract

Novel porous copolymers are disclosed which can be used to prepare ion-exchange resins and polymeric adsorbents. The copolymers comprise a copolymer of at least one monovinylidene monomer and a crosslinking monomer and have a unique cellular pore structure. The cellular structure comprises a macroporous void phase which is dispersed within a continuous copolymer phase. The porous void phase comprises a plurality of cellular void spaces which are at least partially enclosed by walls of the continuous copolymer phase. Also disclosed are processes which can be used to prepare the porous copolymers, as well as ion-exchange resins and polymeric adsorbents using the porous copolymers.

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POROUS COPOLYMERS HAVING A CELLULAR POLYMERIC STRUCTURE SUITABLE FOR PREPARING ION-EXCHANGE RESINS AND ADSORBENTS

The present invention concerns polymers suitable for use in making polymeric adsorbents and ion-exchange resins. More particularly, the invention concerns porous polymers having a unique cellular polymeric structure.

Ion-exchange resins are used by industry to separate chemical species from solutions containing them. Such resins are prepared by substituting various types of functional groups onto a crosslinked polymer matrix. The functional groups are capable of associating with chemical species so as to remove them from solution. Ion-exchange resins may be cat on-, anion-, or chelate-exchange resins, depending on the choice of functional group substituted onto the copolymer matrix. The polymer matrix may also be used in preparing polymeric adsorbents, such as the post-crosslinked adsorbent resins disclosed in U.S. Patent 4,950,332.

The polymer matrix is typically in spheroidal bead form and is generally prepared by suspension polymerization of a finely divided organic phase within a continuous suspending medium. The organic phase comprises monovinylidene monomers like styrene, polyvinylidene monomers like divinylbenzene and a free-radical polymerization initiator. The copolymer beads produced may be microporous, i.e., gel in character, or macroporous, depending upon whether a phase-separating diluent is added to the organic phase. The term "macroporous" refers to the fact that the copolymer has both macropores and and micropores. The terms "microporous," "gel," and "macroporous" are well known in the art and generally describe the nature of the copolymer bead porosity. Microporous copolymer beads have pore sizes on the order of 50 Angstroms (Å) or less, while macroporous copolymer beads have macropores of 100 Å or greater. Gel and macroporous copolymer beads, as well as their preparation, are further discussed in U.S. Patent 4,256,840.

Adsorbent resins based on a post-crosslinked, gel copolymer matrix can be difficult to manufacture as the gel copolymer is, in many instances, susceptible to breakage during the post-crosslinking step employed. Conventional macroporous copolymers generally have better strength relative to gel copolymers and, as a result, are less susceptible to such breakage. However, adsorbent resins derived from such conventional macroporous copolymers may have less adsorption capacity relative to the gel adsorbent resin due to a higher degree of porosity, or void space.

As can be seen, it is desirable to develop a polymerization process for producing copolymer beads which have sufficient strength to resist breakage and are also capable of being converted into resins with sufficient capacity. Such copolymer beads would be advantageous for use in preparing polymeric adsorbents, as well as ion-exchange resins.

The above-described objects are obtained by the novel porous copolymer disclosed herein. More particularly, the present invention concerns a porous copolymer of at least one monovinylidene monomer and a crosslinking monomer present in an amount of from

0.3 to 5 weight percent based on total monomer weight, characterized in that the porous copolymer comprises a cellular pore structure wherein a macroporous void phase is dispersed within a continuous copolymer phase, the void phase comprising a plurality of cellular void spaces which are at least partially enclosed by walls of the continuous copolymer phase. Preferably, the porous copolymer is additionally post-crosslinked in a swollen state in the presence of a Friedel-Crafts catalyst to provide a plurality of bridging moieties which link together adjacent copolymer chains and thereby form rigid micropores.

The above-described porous copolymer can be used in preparing ion-exchange resins and polymeric adsorbents.

Another aspect of the invention is a suspension polymerization process for preparing a porous copolymer having a cellular polymeric structure characterized by contacting in the polymerizable monomer phase at least one monovinylidene monomer, a crosslinking monomer in an amount of from 0.3 to 5 weight percent based on total monomer weight, at least one free-radical polymerization initiator in an amount of from 0.025 to 2 weight percent based on the monomer weight, and a phase-separating diluent present in an amount of from 30 to 80 weight percent based on weight of monomer and diluent at a temperature from 95 to 140°C.

A further aspect of the invention is a process for making a polymeric adsorbent characterized by:

(a) contacting in a suspended polymerizable monomer phase at least one monovinylidene aromatic monomer, a crosslinking monomer in an amount of from 0.3 to 5 weight percent based on total monomer weight, at least one free-radical polymerization initiator in an amount of from 0.025 to 2 weight percent based on the monomer weight, and a phase-separating diluent present in an amount of from 30 to 80 weight percent based on weight of monomer and diluent at a temperature of from 95 to 140°C to produce a porous copolymer having a cellular polymeric structure; and

(b) post-crosslinking the porous copolymer in a swollen state in the presence of a Friedel-Crafts catalyst.

Figure 1 is a scanning electron photomicrograph (SEM) of a cross section from a copolymer having a cellular polymeric structure as disclosed herein.

Figure 2 is a SEM of a cross section taken from a conventional macroporous copolymer.

Figures 3-5 are SEMs of adsorbents prepared from a copolymer having a cellular polymeric structure that may be obtained by the process of Examples 3, 4, and 5, respectively, as more fully described hereinafter.

The porous copolymer has a unique cellular pore structure. This cellular structure is illustrated by Fig. 1 which is a scanning electron photomicrograph of a cross section from such a porous copolymer.

In reference to Fig. 1, it is seen that the cellular structure comprises a macroporous void phase which is dispersed within a continuous copolymer phase. The void phase is dispersed so as to form a plurality of cellular void spaces which are at least partially enclosed by walls of the continuous copolymer phase. As used herein, the term "a plurality of cellular void spaces which are at least partially enclosed by walls of the continuous copolymer phase" is intended to encompass copolymers wherein individual cellular void spaces may, or may not be completely enclosed by the continuous copolymer phase. In the event that the copolymer phase completely encloses the cellular void spaces, the spaces would define a discontinuous void phase and essentially be a "closed cell" as that term is used in describing foams. Where the copolymer phase only partially encloses the cellular void spaces, the spaces would be similar in appearance to an "open cell" as that term is used in discussing foam technology. The terms open cell and closed cell are discussed in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A-11 (VCH Publishers New York, N.Y. 1988) at pages 436-439. Fig. 1 is an example of a closed cell structure.

In Fig. 1, the photomicrograph was obtained by reswelling the copolymer in toluene and, finally, in *iso*-octane. After polymerization, the copolymer was steam distilled to remove *iso*-octane therein that was used as an inert diluent during polymerization. After distillation, the copolymer was dried and swollen to maximum swellability in an excess amount of toluene. Thereafter, *iso*-octane was gradually added to the swollen copolymer such that the toluene in the copolymer was exchanged with *iso*-octane. The copolymer was then dried and the photomicrograph taken thereafter. In Figs. 2-5, the photomicrographs were taken with the respective copolymer or resins being in a dry state. The copolymer or resins were not reswollen, as described above.

The cellular void spaces within the copolymer are essentially polygonal in shape with a diameter that generally ranges from 100 to 2000 Å. When post-crosslinked or functionalized as described hereinafter, the cellular void spaces may appear less polygonal in shape, and in many instances will appear essentially spherical.

This cellular structure is substantially different when compared to the structure of a conventional macroporous or macroreticular copolymer. Fig. 2 is another scanning electron photomicrograph which illustrates a cross section from a typical macroporous or macroreticular copolymer. Macropores are seen as channels, or veins, of continuous void phase that are disposed between a continuous copolymer phase. Fig. 2 illustrates that such conventional macroporous or macroreticular copolymers have a copolymer phase consisting of an agglomerated mass of minute spherical gel copolymer particles, as described in U.S. Patent 4,224,415

In general, the copolymers of the invention are preferably prepared by suspension polymerization methods wherein a monomer mixture is suspended within an agitated, continuous suspending medium, as generally discussed in U.S. Patents 4,256,840 and

4,382,124. The monomer mixture comprises at least one monovinylidene monomer, a crosslinking monomer, an effective amount of a phase-separating diluent, and an effective amount of a free-radical polymerization initiator. The suspending medium may contain one or more suspending agents commonly employed in the art. Polymerization is conducted by maintaining the suspension at a polymerizing temperature until reaching a desired degree of conversion of monomer to copolymer. Another suitable polymerization method is generally described in U.S. Patent 4,444,961. Specific parameters required for obtaining the cellular pore structure are described below.

The cellular structure is obtained by using an effective amount of a phase-separating diluent with minor amounts of crosslinking monomer. It is also believed that the morphology of the cellular structure is promoted by adjusting the amount of free-radical polymerization initiator and the polymerization temperature.

The monomers employed are addition polymerizable ethylenically unsaturated compounds. Such monomers are well known and reference is made to Polymer Processes, edited by Calvin E. Schildknecht, published in 1956 by Interscience Publishers, Inc., New York, Chapter III. "Polymerization in Suspension" at pp. 69-109 for purposes of illustration.

In Table II on pp. 78-81 of Schildknecht are listed diverse kinds of monomers suitable for practicing this invention. Of such ethylenically unsaturated monomers, of particular interest are water-insoluble monovinylidene monomers, particularly monovinylidene aromatic monomers such as styrene, vinyl naphthalene, alkylene-substituted styrenes (particularly monoalkyl-substituted styrenes such as vinyltoluene and ethylstyrene) and halo-substituted styrenes, such as bromo- or chlorostyrene and vinylbenzylchloride; acrylic monomers, such as methyl acrylate, ethyl acrylate, methyl ethyl acrylate, or methyl metnacrylate; and mixtures of one or more of said monomers. Preferred monovinylidene aromatic monomers include styrene, monoalkyl-substituted styrenes, and halo-substituted styrenes. Also suitable are diverse polyvinylidene compounds which may be employed as crosslinking monomers, such as polyvinylidene aromatics like divinylbenzene, divinyltoluene, divinylxylene, divinylnaphthalene, trivinylbenzene, divinyldiphenyl ether, divinyldiphenylsulfone, as well as diverse alkylene diacrylates and alkylene dimethacrylates. Preferred crosslinking monomers are divinylbenzene, trivinylbenzene, and ethylene glycol dimethacrylate.

Relatively minor amounts of crosslinking monomer assist with formation of a cellular structure. For a preferred styrene-divinylbenzene monomer system employing a C_4 alkane diluent, the amount of crosslinking monomer is preferably from 0.3 to 5 weight percent and more preferably from 1 to 4 weight percent based on total weight of monomers employed. Notwithstanding the above, it should be understood that such amounts of crosslinking monomer may not be necessary for other monomer/diluent systems.

Phase-separating diluents used in preparing the porous copolymers are those which are a solvent for the monomers employed, but are non-solvents for the resulting copolymer. As such, phase separation between the resulting copolymer and the monomer phase occurs as the copolymer forms. Suitable phase-separating diluents are organic solvents which are substantially inert with respect to the suspending medium, monomers, and resulting copolymer. Generally, organic solvents having boiling points of at least 60°C are suitable and include aromatic hydrocarbons, aliphatic hydrocarbons, halogenated hydrocarbons, and aliphatic alcohols. Examples of suitable diluents are hexane, heptane, *iso*-octane (2,2,4-trimethylpentane), benzene, toluene, xylene, *tert*-amyl alcohol, *n*-butanol, sec-butanol, 2-ethylhexanol, and decanol.

The amount of phase-separating diluent employed is an important parameter for obtaining a cellular structure. In general, for a given proportion of monovinylidene monomer, crosslinking monomer and initiator, and holding polymerization conditions constant, when the amount of diluent is relatively low the resulting copolymer structure is microporous, i.e., it has pores generally less than 50 Å in size. As the amount of diluent is increased, it is believed that a transition point is reached wherein phase separation of the copolymer from the monomer/diluent phase occurs and the copolymer structure gradually changes from being essentially all microporous to one having a conventional macroporous or macroreticular structure, as illustrated by Fig. 2. As the amount of diluent is increased beyond this initial transition point, it is believed that a second transition point is reached wherein phase separation is more pronounced, and thereby gradually results in a cellular polymeric structure, as illustrated by Fig. 1. The cellular copolymers are obtained by using an amount of diluent which is sufficient to reach this second transition point.

As those skilled in the art can appreciate, the amount of phase-separating diluent necessary to obtain a cellular structure varies with the choice of monomers, the amount of crosslinking monomer, and diluent employed for a given polymerization. As a result, a sufficient amount of diluent must be determined more or less empirically for a given monomer-diluent system. In a preferred styrene-divinylbenzene monomer system employing a C_{6-10} alkane diluent, such as hexane, heptane, or *iso*-octane, the amount of phase-separating diluent required is desirably from 30 to 80 weight percent based on the weight of the monomers and diluent. In this system, the amount of diluent is preferably from 35 to 50 weight percent.

The free-radical initiator may be any one or a combination of conventional initiators for generating free-radicals in the polymerization of ethylenically unsaturated monomers. Representative initiators are UV radiation and chemical initiators, such as azo-compounds like azobisisobutyronitrile; and peroxygen compounds such as benzoyl peroxide, *t*-butylperoctoate, *t*-butylperbenzoate and *iso*-propylpercarbonate.

The free-radical initiator employed can also be used to promote formation of a cellular structure. Generally, for a given proportion of reactants and polymerization

conditions, an increase in the amount of initiator can increase the size of the cells which are formed. This result is exemplified by comparison of Figs. 4 and 5, wherein the respective examples differ essentially in the amount of initiator employed. An effective amount of free-radical initiator to obtain a cellular structure is from 0.005 to 10, and preferably from 0.025 to 2 weight percent, based on total monomer weight.

The polymerization temperature is also a parameter which can be used to promote formation of a cellular structure. The polymerization temperature is preferably higher than those typically used in suspension polymerization of ethylenically unsaturated monomers. The temperature is preferably from 95 to 140°C, and more preferably from 100 to 120°C.

In the preferred suspension polymerization methods, the monomer phase is suspended within an agitated suspending medium which comprises a liquid that is substantially immiscible with the monomer phase. Due to the fact that most monomers employed are primarily non-polar organic compounds, a preferred suspending medium is water. Generally, the suspending medium is employed in an amount from 30 to 70, and preferably from 35 to 50 weight percent based on total weight of the monomer mixture and suspending medium. Various suspending agents are conventionally employed to assist with maintaining a relatively uniform suspension of monomer droplets within the suspending medium. Illustrative suspending agents are gelatin, polyvinyl alcohol, magnesium hydroxide, hydroxyethylcellulose, methylcelluloses, and carboxymethylmethylcellulose. The amount of suspending agent used can vary widely depending on the monomers and suspending agents employed.

The porous copolymer beads obtained by suspension polymerization methods are essentially spheroidal in shape and have diameters which can vary widely, as those skilled in the art can appreciate. For most uses, bead diameters may be from 50 to 5000 μm.

An adsorbent resin can be prepared from the resulting copolymer by post-crosslinking individual polymer chains after polymerization. Post-crosslinking may be achieved by swelling the copolymer with a swelling agent and subsequently reacting the copolymer with a polyfunctional alkylating or acylating agent, as is described in U.S. Patents 4,191,813 and 4,263,407.

To obtain an adsorbent such as that described in U.S. Patent 4,950,332, the porous copolymer beads may be post-crosslinked in a swollen state in the presence of a Friedel-Crafts catalyst to introduce rigid microporosity (pores with a diameter of 50 Å or less) into the copolymer. In this type of process, the copolymer should be prepared from a monomer mixture comprising a monovinylidene aromatic monomer, as the post-crosslinking step requires the presence of aromatic rings on individual polymer chains. Small amounts of non-aromatic monovinylidene monomers, preferably less than 30 weight percent based on monomer weight, can be employed in the monomer mixture being polymerized, but it is less desirable to do so as the resulting adsorbents may have decreased amounts of surface area and microporosity. Post-

crosslinking of the copolymer while it is in a swollen state displaces and rearranges adjacent polymer chains, thereby causing an increase in the number of micropores. This rearrangement serves to increase overall porosity and surface area of the copolymer, while also decreasing the average pore size. Post-crosslinking also serves to impart rigidity to the copolymer structure, which is important for providing enhanced physical and dimensional stability to the copolymer.

A preferred method for post-crosslinking the copolymer comprises haloalkylating the copolymer with a haloalkylating agent, swelling the resulting haloalkylated copolymer with an inert swelling agent, and thereafter maintaining the swollen, haloalkylated copolymer at a temperature and in the presence of a Friedel-Crafts catalyst such that haloalkyl moieties on the copolymer react with an aromatic ring of an adjacent copolymer chain to form a bridging moiety. It is also preferred to substantially remove excess haloalkylating agent and/or solvents employed in haloalkylating the copolymer prior to post-crosslinking to obtain good quality copolymer and high surface area. This type of method is described in U.S. Patent 4,950,332.

In general, haloalkylation is achieved by contacting the copolymer with a haloalkylating agent under conditions sufficient to substitute the copolymer with haloalkyl moieties. A preferred haloalkylating agent is chloromethyl methyl ether. Preferably, the copolymer is haloalkylated by first swelling it under non-reactive conditions with the haloalkylating agent and an effective amount of a Friedel-Crafts catalyst. The haloalkylating agent advantageously has the Friedel-Crafts catalyst incorporated therein. The swollen copolymer beads are then maintained at a temperature sufficient to react the haloalkylating agent with the copolymer beads until achieving a desired degree of reaction. In preparing the adsorbent materials, the porous copolymer is preferably halomethylated and most preferably chloromethylated. Methods for haloalkylating copolymer particles are known. Illustrative of such are U.S. Patents 2,642,417; 2,960,480; and 2,992,544. Chloromethyl methyl ether is commonly employed as a haloalkylating agent. After haloalkylation, it is preferred to remove excess haloalkylating agent and/or solvents used during haloalkylation. This can be accomplished by any method, such as washing with an organic solvent like methanol, or drying.

After haloalkylation, the copolymer is contacted with a swelling agent to expand the copolymer structure. Suitable swelling agents are solvents which are substantially inert during post-crosslinking of the haloalkylated copolymer and include chlorinated hydrocarbons, such as dichloroethane, chlorobenzene, dichlorobenzene, ethylene dichloride, methylene chloride, and propylene dichloride; or nitrogen-substituted aromatics, like nitrobenzene. A preferred swelling agent is dichloroethane. Advantageously, the copolymer is allowed to swell in an excess amount of the swelling agent for at least 30 minutes. Preferably, the copolymer is contacted with the swelling agent for a time sufficient to substantially attain equilibrium with respect to swelling of the particular swelling agent employed. It is also generally convenient to dissolve the Friedel-Crafts catalyst employed in the subsequent post-crosslinking reaction within the swelling agent.

Once swollen, the haloalkylated copolymer is maintained at a temperature and in the presence of a Friedel-Crafts catalyst such that the bridging moieties are formed by reaction of the haloalkyl moieties with an adjacent aromatic ring. Suitable catalysts are those discussed in connection with haloalkylation. Preferably, the reaction temperature can be from 20 to 180°C for a period of at least 0.5 hours. More preferably, the temperature is from 60 to 85°C. Where the copolymer is chloromethylated, reaction of a chloromethyl group with the aromatic ring of an adjacent copolymer chain results in formation of a methylene bridge, i.e., a -CH2- moiety, between two copolymer chains. After formation of the bridging moiety, the swelling agent is removed by conventional methods, such as solvent extraction, washing, drying, or a combination thereof. If a drying step is used, it is preferred to avoid an oxygen-containing atmosphere at temperatures above normal room temperature.

After post-crosslinking, the resulting polymeric adsorbent desirably has a specific surface area of at least 600 square meters per gram ("m^2/g") of dry adsorbent resin, preferably at least 1000, more preferably at least 1200 m^2/g. Specific surface area may be determined by well-known BET nitrogen adsorption techniques.

In terms of porosity, the adsorbent preferably has from 0.5 to 1.5 cubic centimeters of pore volume per gram of adsorbent material ("cc/g"). Most preferably, the adsorbent has from 0.7 to 1.3 cc/g of porosity.

If desired, the porous copolymer beads may be converted to ion-exchange resins by functionalizing them with ion-exchange or chelate-exchange functional groups. Techniques for converting copolymers to anion-, cation-, and chelate-exchange resins are known.

In preparing anion- and chelate-exchange resins from poly(vinylaromatic) copolymer beads, such as cross-linked polystyrene beads, the beads are first haloalkylated, preferably chloromethylated, and the anion- or chelate-exchange groups are subsequently substituted onto the haloalkylated copolymer. The porous copolymer beads may be haloalkylated by the methods previously described.

Anion- or chelate-exchange resins may be prepared from the haloalkylated beads by contact with an amine compound capable of replacing the halogen of the haloalkyl group with an amine-based functional group. Suitable compounds and methods for preparing such resins are also illustrated in the patents previously discussed concerning haloalkylation.

Weak-base anion resins may be prepared by contacting the haloalkylated copolymer beads with ammonia, a primary amine, a secondary amine, or polyamines like ethylene diamine or propylene diamine. Commonly employed primary and secondary amines include methylamine, ethylamine, butylamine, cyclohexylamine, dimethylamine, and diethylamine.

Strong-base anion resins may be prepared by contact with tertiary amines, such as trimethylamine, triethylamine, dimethylisopropanolamine, or ethylmethylpropylamine

Chelate resins may be prepared, for example, by contacting the haloalkylated copolymer beads with an aminopyridine compound, such as a 2-picolylamine. Chelate-exchange resins may also be prepared by contacting the haloalkylated copolymer beads with a primary amine to initially convert the copolymer beads to a weak-base anion-exchange resin followed by contact with a carboxyl-containing compound, like chloroacetic acid, as described in U.S. Patent 2,888,441.

Amination typically comprises contacting the haloalkylated copolymer beads with an amine compound at a temperature of from 25°C to 150°C for at least 1 hour.

Cation-exchange resins may be prepared from the copolymer beads using methods illustrated by U.S. Patents 3,266,007; 2,500,149; 2,631,127; 2,664,801; and 2,764,564. In general, strong acid resins are prepared by reacting the copolymer with a sulfonating agent such as sulfuric acid, chlorosulfonic acid, or sulfur trioxide. Contact with the sulfonating agent can be conducted neat, or with a swelling agent. Contact may be conducted at temperatures from 0°C to 150°C.

The resulting cation-exchange resin may be converted to a desired metal salt form by contact with an aqueous solution of a salt or base containing the desired metal counterion. For example, the resin can be converted to its calcium form by contact with a $CaCl_2$ or $Ca(OH)_2$ solution. The resin can be converted to other forms in like manner using suitable water-soluble salts of the desired metal.

The following examples are intended to illustrate the invention. All parts and percentages are by weight and all temperatures are in degrees Celsius (°C), unless otherwise indicated.

Examples 1-10

Examples 1-10 concern preparation of copolymers having a cellular polymeric structure and also preparation of adsorbents by post-crosslinking the copolymers.

A suitable polymerization kettle equipped with agitation is charged with a monomer phase composed of measured amounts of styrene, a divinylbenzene mixture obtained from The Dow Chemical Company containing 55 weight percent divinylbenzene and 45 weight percent ethylvinylbenzene based on weight of the mixture, commercial grade iso-octane, and *t*-butylperbenzoate (*t*-BPB) and *t*-butylperoctoate (*t*-BPO) as free-radical initiators. The proportion of each component, in terms of a weight percentage, employed in a particular example is listed in Table I. After charging the kettle with the monomer phase, an aqueous phase composed of water, sodium dichromate, and carboxymethylmethylcellulose (CMMC) is added. The proportion of monomer phase to aqueous phase employed is 1:1. The proportion of specific aqueous phase components, also in terms of a weight percentage, are listed in Table I.

TABLE I - MATERIALS AND CONDITIONS EMPLOYED IN EXAMPLES 1-10

Example No.	Styrene (%)[1]	DVB (%)[1]	Diluent (%)[2]	t-BPO (%)[3]	t-BPB (%)[3]	Sodium Dichromate (%)4	CMMC (%)4	Initial Temp (°C)	Initial Time (hrs)	Finish Temp (°C)	Finish Time (hrs)
1	99.25	0.75	42	0	0.2	0.17	0.2	100	18	110	2
2	98.5	1.5	35	0.1	0.2	0.17	0.2	110	9	-	-
3	98.5	1.5	35	0.5	0.2	0.17	0.2	110	9	-	-
4	98.5	1.5	40	0.1	0.2	0.17	0.2	110	9	-	-
5	98.5	1.5	40	0.5	0.2	0.17	0.2	110	9	-	-
6	98.5	1.5	45	0.025	0.2	0.17	0.2	110	9	-	-
7	98.5	1.5	45	0.1	0.2	0.17	0.2	110	9	-	-
8	98.5	1.5	45	0.15	0.2	0.17	0.2	80	10	110	5
9	98.5	1.5	50	0.5	0.2	0.17	0.2	110	9	-	-
10	98	2	45	0.05	0.2	0.17	0.2	110	9	-	-

1 % DVB or styrene = $\frac{\text{weight styrene or divinylbenzene}}{\text{total monomer weight}}$

2 % Diluent = $\frac{\text{weight diluent}}{\text{total weight of monomers + diluent}}$

3 % t-BPB or t-BPO = $\frac{\text{weight of initiator}}{\text{total monomer weight}}$

4 % Sodium Dichromate or CMMC = $\frac{\text{weight of component}}{\text{total weight of aqueous phase}}$

After adding the monomer and aqueous phases, the kettle is sealed and purged with nitrogen. Agitation is initiated to size the monomer phase into droplets. The kettle contents are heated to an initial polymerization temperature (Initial Temperature) as indicated in Table I and, subsequently, maintained at this temperature for a time (Initial Time) also indicated in Table I to obtain porous copolymer beads. In two of the examples, the respective polymerizations are concluded by increasing the temperature to a temperature (Finish Temperature) and for a time (Finish Time) as indicated in Table I to more fully complete polymerization. The kettle contents are then allowed to cool to room temperature. The porous copolymer beads are recovered from the kettle, washed with water, and iso-octane is removed by steam distillation. The beads are finally allowed to dry at room temperature.

The porous copolymer beads are then post-crosslinked by substituting the copolymer with chloromethyl groups, washing the beads to remove excess haloalkylating agent, swelling the chloromethylated copolymer beads with an inert swelling agent, and then reacting the chloromethyl groups in the presence of a Friedel-Crafts catalyst. For each example, a 30 gram (g) portion of the respective beads and 500 milliliters (ml) of chloromethyl methyl ether (CMME) are placed in a 1 liter (L) reactor. The copolymer beads are allowed to swell with the CMME under moderate agitation for 30 minutes (min). Thereafter, 9 g of ferric chloride is added to the reactor. The reactor contents are then maintained at a temperature of 45°C for 2.5 hours (hr). The reactor contents are cooled and washed with an excess amount of methanol to remove the CMME from the beads. Excess liquid is removed from the reactor and the chloromethylated beads are again washed with methanol and finally recovered from the reactor.

The resulting methanol-moist chloromethylated beads are swollen with an excess amount of 1,2-dichloroethane (EDC) in a 1 L reactor. Thereafter, the reactor contents are heated to distill off any residual amount of methanol from the beads. Upon reaching an overhead product temperature of 82°C, distillation is discontinued and the beads are allowed to cool to 20°C. A 9 g amount of ferric chloride catalyst is added to the reactor and the cooled beads are allowed to contact the catalyst for 30 min. The beads are then heated and maintained at a temperature of 80°C for 3 hrs. After cooling the resulting adsorbent beads to room temperature, the EDC is extracted by rinsing the beads five times with methanol. The adsorbent beads are dried overnight in an oven at 120°C.

After drying, the beads are analyzed to determine the various physical properties listed in Table II. The presence of a cellular polymeric structure is also confirmed by scanning electron microscopy. Figs. 4, 5, and 6 illustrate the structures obtainable from the methods of Examples 3, 4, and 5 respectively. The figures illustrate a structure wherein a discontinuous porous void phase is dispersed within a continuous copolymer phase.

TABLE II - PHYSICAL PROPERTY DATA FOR EXAMPLES 1-10

Example No.	Vol. Avg. Diameter of Adsorbent (μm)	Crush Strength (g/bead)	Whole Beads (%)	Specific Surface Area (m^2/g)	Total Porosity (cc/g)	Porosity >100Å (cc/g)
1	799	240	99	1150	1.207	0.400
2	840	612	99	1278	0.934	0.074
3	670	670	99	1310	1.174	0.050
4	670	456	98	1376	1.059	0.040
5	666	666	97	1220	1.102	0.055
6	662	485	99	1409	1.255	0.139
7	1521	1147	96	1250	1.025	0.092
8	780	1464	100	1158	0.961	0.223
9	584	666	99	895	0.730	0.225
10	808	1110	95	986	0.901	0.254

Crush Strength is determined by taking a representative sample of at least about 20 beads from a given sample of adsorbent or copolymer beads, and determining the force, in grams, needed to fracture each bead using a Chatillon Scale, Model DPP-1KG, available from J. Chatillon & Sons Company. Crush strength is reported as the average of the force measurements obtained for the 20 beads.

Volume average particle diameters are determined by use of a particle size analyzer obtained from the HIAC-Royco Company.

The number of whole beads, expressed as a percent, is determined by microscopic examination of a representative sample of at least 200 beads. The number of substantially spherical beads in the sample is determined and a percentage is calculated therefrom.

Porosity and specific surface area data are determined by well-known BET nitrogen adsorption techniques.

Examples 11-12

The procedure of Examples 1-10 is substantially repeated, except that methyl methacrylate (MMA) is added to the monomer phase being polymerized.

The proportions of materials added to the kettle and polymerization temperature is listed in Table III. The proportion of monomer phase to aqueous phase employed is also 1:1. The physical properties of the resulting adsorbents are listed in Table IV.

TABLE III - MATERIALS AND CONDITIONS EMPLOYED IN EXAMPLES 11 and 12

Example No.	Styrene (%)[1]	MMA (%)[1]	DVB (%)[1]	Diluent (%)[2]	*t*-BPO (%)[3]	*t*-BPB (%)[3]	Sodium Dichromate (%)4	CMMC (%)4	Temp (°C)
11	88.5	10	1.5	35	0.1	0.2	0.17	0.2	110
12	64.5	34	1.5	45	0.05	0.2	0.17	0.2	110

1 % monomer = $\frac{\text{weight of an individual monomer}}{\text{total monomer weight}}$

2 % Diluent = $\frac{\text{weight diluent}}{\text{total weight of monomers + diluent}}$

3 % t-BPB or t-BPO = $\frac{\text{weight of component}}{\text{total monomer weight}}$

4 % Sodium Dichromate or CMMC = $\frac{\text{weight of component}}{\text{total weight of aqueous phase}}$

TABLE IV - PHYSICAL PROPERTY DATA FOR EXAMPLES 11-12

Example No.	Vol. Avg. Diameter of Adsorbent (μm)	Crush Strength (g/bead)	Whole Beads (%)	Specific Surface Area (m^2/g)	Total Porosity (cc/g)
11	802	429	82	1232	0.542
12	*	1812	97	454	0.895

*not determined

Example 13

Example 13 concerns preparation of a post-crosslinked, anion-exchange resin from a copolymer having a cellular polymeric structure.

A 3 L polymerization kettle equipped with agitation is charged with a monomer phase composed of 744.9 g of styrene, 10.1 g of a divinylbenzene mixture obtained from The Dow Chemical Company containing 55 weight percent divinylbenzene and 45 weight percent ethylvinylbenzene based on weight of the mixture (a divinylbenzene content of 0.75 weight percent based on total monomer weight), 546 g of *iso*-octane (42 percent by weight based on weight of monomer and diluent), and 7.6 g of *t*-butylperbenzoate (*t*-BPB) as a free-radical initiator. After charging the kettle with the monomer phase, an aqueous phase composed of 1040 g of deionized water, 3.3 g of a 67 percent aqueous sodium dichromate solution, and 260 g of a 1 percent aqueous CMMC solution is added.

After adding the monomer and aqueous phases, the kettle is sealed and purged with nitrogen. Agitation is initiated to size the monomer phase into droplets. The kettle contents are heated to a temperature of 100°C and maintained at that temperature for 18 hrs. The polymerization was completed by heating the kettle contents to a temperature of 110°C and maintaining the temperature for 2 hrs. The kettle contents are then allowed to cool to room temperature. The beads are recovered from the kettle, washed with water, and *iso*-octane is removed therefrom by steam distillation. The beads are allowed to dry at room temperature. The presence of a cellular structure is confirmed by scanning electron microscopy.

A 30 g portion of the copolymer beads is placed with 600 ml of CMME in a 1 L reactor. The copolymer beads are allowed to swell with the CMME under moderate agitation for 30 min. Thereafter, 9 g of ferric chloride is added to the reactor. The reactor contents are then maintained at a temperature of 45°C for 3 hrs. The reactor contents are cooled and washed with an excess amount of methanol to remove the CMME from the beads. Excess liquid is removed from the reactor and the chloromethylated beads are again washed with methanol.

The resulting methanol-moist chloromethylated beads are swollen with an excess amount of EDC in a 1 L reactor. Thereafter, the reactor contents are heated to distill off any residual amount of methanol from the beads. Upon reaching an overhead product temperature of 82°C, distillation is discontinued and the beads are allowed to cool to 20°C. A 9 g amount of ferric chloride catalyst is added to the reactor and the cooled beads are allowed to contact the catalyst for 30 min. The beads are then heated and maintained at a temperature of 80°C for 3 hrs. After cooling the resulting adsorbent beads to room temperature, the EDC is extracted by rinsing the beads five times with methanol. The adsorbent beads are dried overnight in an oven at 120°C.

The copolymer beads are then aminated with dimethylamine. An excess amount of aqueous dimethylamine solution is added to the beads in a 1 L reactor, along with 500 g of

water. The beads are then heated to a temperature of 70°C and maintained at that temperature for 1 hr.

The physical properties of the resulting resin are determined as in Examples 1-10. The resin has the following properties: a volume average particle diameter of 799 µm, 99 percent whole beads, 240 g/bead crush strength, and a water retention capacity of 77 percent. Water retention capacity is determined by well-known methods.

CLAIMS:

1. A porous copolymer of at least one monovinylidene monomer and a crosslinking monomer present in an amount of from 0.3 to 5 weight percent based on total monomer weight, characterized in that the porous copolymer comprises a cellular pore structure wherein a macroporous void phase is dispersed within a continuous copolymer phase, the void phase comprising a plurality of cellular void spaces which are at least partially enclosed by walls of the continuous copolymer phase.

2. The porous copolymer of Claim 1 in which at least one monovinylidene monomer is styrene, vinylbenzyl chloride, vinyltoluene or ethylstyrene and in which the crosslinking monomer is divinylbenzene, trivinylbenzene or ethylene glycol dimethacrylate.

3. The porous copolymer of Claims 1 or 2 in which the cellular void spaces have diameters from 100 to 2000Å.

4. The porous copolymer of Claim 2 in which the cellular void spaces are completely enclosed by walls of the continuous copolymer phase.

5. A suspension polymerization process for preparing a porous copolymer of Claim 1 having a cellular polymeric structure characterized by contacting in the polymerizable monomer phase at least one monovinylidene monomer, a crosslinking monomer in an amount of from 0.3 to 5 weight percent based on total monomer weight, at least one free-radical polymerization initiator in an amount of from 0.025 to 2 weight percent based on the monomer weight, and a phase-separating diluent present in an amount of from 30 to 80 weight percent based on weight of monomer and diluent at a temperature from 95 to 140°C.

6. The process of Claim 5 in which at least one monovinylidene monomer is styrene, vinylbenzyl chloride, vinyltoluene or ethylstyrene and in which the crosslinking monomer is divinylbenzene, trivinylbenzene or ethylene glycol dimethacrylate.

7. The process of Claim 5 in which at least one free-radical polymerization initiator is *t*-butylperoctoate, *t*-butylperbenzoate, benzoyl peroxide, or *iso*-propylpercarbonate.

8. The process of Claim 5 in which the phase-separating diluent is a C_{6-12} alkane.

9. The porous copolymer produced by the process of any one of Claims 5-8.

10. A polymeric adsorbent characterized in that it comprises a copolymer of at least one monovinylidene aromatic monomer and a crosslinking monomer present in an amount of from 0.3 to 5 weight percent based on total monomer weight and having a cellular pore structure wherein a macroporous void phase is dispersed within a continuous copolymer phase, the void phase comprising a plurality of cellular void spaces which are at least partially enclosed by walls of the continuous copolymer phase, the porous copolymer being post-crosslinked in a swollen state in the presence of a Friedel-Crafts catalyst to provide a plurality of bridging moieties which link together adjacent copolymer chains and thereby form rigid micropores.

11. The adsorbent of Claim 10 in which the bridging moieties are $-CH_2-$ moieties.

12. The adsorbent of Claims 10 or 11 in which at least one monovinylidene monomer is styrene, vinylbenzyl chloride, vinyltoluene or ethylstyrene and in which the crosslinking monomer is divinylbenzene, trivinylbenzene or ethylene glycol dimethacrylate.

13. The adsorbent of Claim 12 in which the cellular void spaces have diameters from 100 to 2000Å.

14. The adsorbent of Claim 12 in which the cellular void spaces are completely enclosed by walls of the continuous copolymer phase.

15. A process for making a polymeric adsorbent having cellular pore structure characterized by:

(a) contacting in a suspended polymerizable monomer phase at least one monovinylidene aromatic monomer, a crosslinking monomer in an amount of from 0.3 to 5 weight percent based on total monomer weight, at least one free-radical polymerization initiator in an amount of from 0.025 to 2 weight percent based on the monomer weight, and a phase-separating diluent present in an amount of from 30 to 80 weight percent based on weight of monomer and diluent at a temperature of from 95 to 140°C to produce a porous copolymer having a cellular polymeric structure; and

(b) post-crosslinking the porous copolymer in a swollen state in the presence of a Friedel-Crafts catalyst.

16. The process of Claim 15 in which post-crosslinking is characterized by:

removing the phase-separating diluent from the porous copolymer;

contacting the copolymer with a haloalkylating agent under conditions sufficient to substitute the copolymer with haloalkyl moieties;

removing any excess haloalkylating agent from the copolymer;

swelling the copolymer with an inert swelling agent;

maintaining the swollen copolymer at a temperature and in the presence of a Friedel-Crafts catalyst such that individual haloalkyl moieties on a copolymer chain react with an aromatic ring of an adjacent copolymer chain to form a bridging moiety; and

removing the swelling solvent from the copolymer.

17. The process of Claim 16 in which the haloalkylating agent is chloromethyl methyl ether.

18. The process of Claim 16 in which the bridging moiety is a $-CH_2-$ moiety.

19. The process of Claim 16 in which the swelling solvent is 1,2-dichloroethane.

20. The polymeric adsorbent produced by the process of any one of Claims 15-19.

AMENDED CLAIMS

[received by the International Bureau on 2 February 1994 (02.02.94); original claims 2 and 13 cancelled; claims 1-20 amended and renumbered as claims 1-18 (2 pages)]

1. A porous copolymer of at least one monovinylidene monomer and a crosslinking monomer present in an amount of from 0.3 to 5 weight percent based on total monomer weight, characterized in that the porous copolymer comprises a cellular pore structure wherein a macroporous void phase is dispersed within a continuous copolymer phase, the void phase comprising a plurality of cellular void spaces having diameters from 100 to 2000Å which are at least partially enclosed by walls of the continuous copolymer phase.

2. The porous copolymer of Claim 1 in which at least one monovinylidene monomer is styrene, vinylbenzyl chloride, vinyltoluene or ethylstyrene and in which the crosslinking monomer is divinylbenzene, trivinylbenzene or ethylene glycol dimethacrylate.

3. The porous copolymer of Claim 2 in which the cellular void spaces are completely enclosed by walls of the continuous copolymer phase.

4. A suspension polymerization process for preparing a porous copolymer of Claim 1 having a cellular polymeric structure characterized by contacting in the polymerizable monomer phase at least one monovinylidene monomer, a crosslinking monomer in an amount of from 0.3 to 5 weight percent based on total monomer weight, at least one free-radical polymerization initiator in an amount of from 0.025 to 2 weight percent based on the monomer weight, and a phase-separating diluent present in an amount of from 30 to 80 weight percent based on weight of monomer and diluent at a temperature from 95 to 140°C.

5. The process of Claim 4 in which at least one monovinylidene monomer is styrene, vinylbenzyl chloride, vinyltoluene or ethylstyrene and in which the crosslinking monomer is divinylbenzene, trivinylbenzene or ethylene glycol dimethacrylate.

6. The process of Claim 4 in which at least one free-radical polymerization initiator is *t*-butylperoctoate, *t*-butylperbenzoate, benzoyl peroxide, or *iso*-propylpercarbonate.

7. The process of Claim 4 in which the phase-separating diluent is a C_{6-10} alkane.

8. The porous copolymer produced by the process of any one of Claims 4-7.

9. A polymeric adsorbent characterized in that it comprises a copolymer of at least one monovinylidene aromatic monomer and a crosslinking monomer present in an amount of from 0.3 to 5 weight percent based on total monomer weight and having a cellular pore structure wherein a macroporous void phase is dispersed within a continuous copolymer phase, the void phase comprising a plurality of cellular void spaces having diameters from 100 to 2000Å which are at least partially enclosed by walls of the continuous copolymer phase, the porous copolymer being post-crosslinked in a swollen state in the presence of a Friedel-Crafts catalyst to provide a plurality of bridging moieties which link together adjacent copolymer chains and thereby form rigid micropores.

10. The adsorbent of Claim 9 in which the bridging moieties are $-CH_2-$ moieties.

11. The adsorbent of Claims 9 or 10 in which at least one monovinylidene monomer is styrene, vinylbenzyl chloride, vinyltoluene or ethylstyrene and in which the crosslinking monomer is divinylbenzene, trivinylbenzene or ethylene glycol dimethacrylate.

12. The adsorbent of Claim 11 in which the cellular void spaces are completely enclosed by walls of the continuous copolymer phase.

13. A process for making a polymeric adsorbent having cellular pore structure characterized by:

(a) contacting in a suspended polymerizable monomer phase at least one monovinylidene aromatic monomer, a crosslinking monomer in an amount of from 0.3 to 5 weight percent based on total monomer weight, at least one free-radical polymerization initiator in an amount of from 0.025 to 2 weight percent based on the monomer weight, and a phase-separating diluent present in an amount of from 30 to 80 weight percent based on weight of monomer and diluent at a temperature of from 95 to 140°C to produce a porous copolymer having a cellular polymeric structure; and

(b) post-crosslinking the porous copolymer in a swollen state in the presence of a Friedel-Crafts catalyst.

14. The process of Claim 13 in which post-crosslinking is characterized by:

removing the phase-separating diluent from the porous copolymer;

contacting the copolymer with a haloalkylating agent under conditions sufficient to substitute the copolymer with haloalkyl moieties;

removing any excess haloalkylating agent from the copolymer;

swelling the copolymer with an inert swelling agent;

maintaining the swollen copolymer at a temperature and in the presence of a Friedel-Crafts catalyst such that individual haloalkyl moieties on a copolymer chain react with an aromatic ring of an adjacent copolymer chain to form a bridging moiety; and

removing the swelling solvent from the copolymer.

15. The process of Claim 14 in which the haloalkylating agent is chloromethyl methyl ether.

16. The process of Claim 14 in which the bridging moiety is a $-CH_2-$ moiety.

17. The process of Claim 14 in which the swelling solvent is 1,2-dichloroethane.

18. The polymeric adsorbent produced by the process of any one of Claims 13-17.

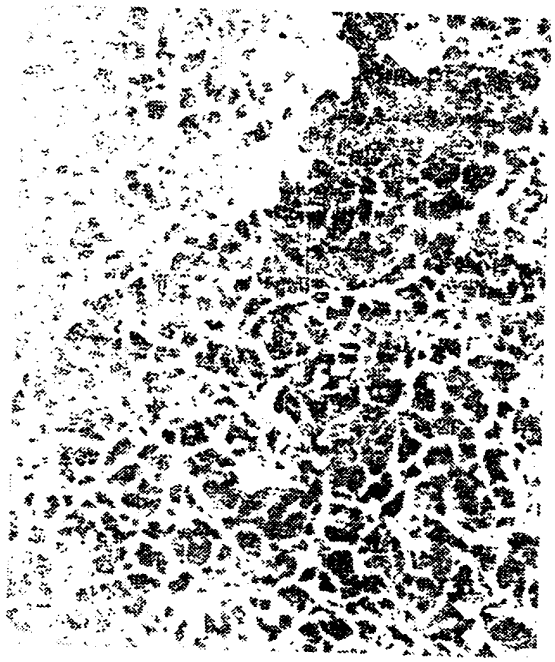

Fig. 1

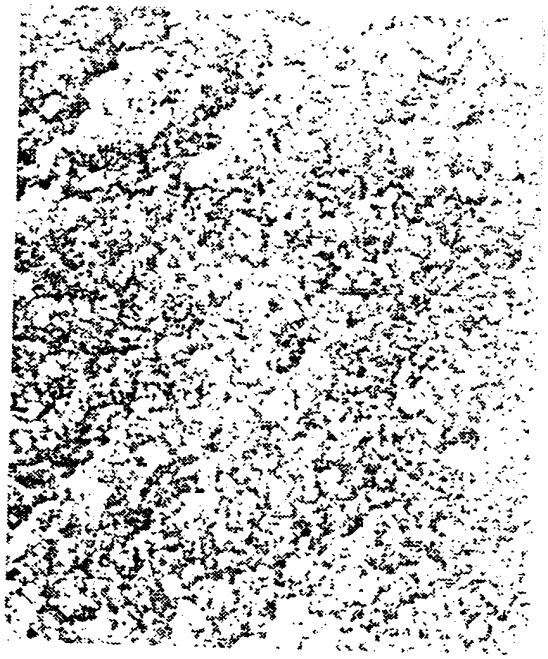

Fig. 2

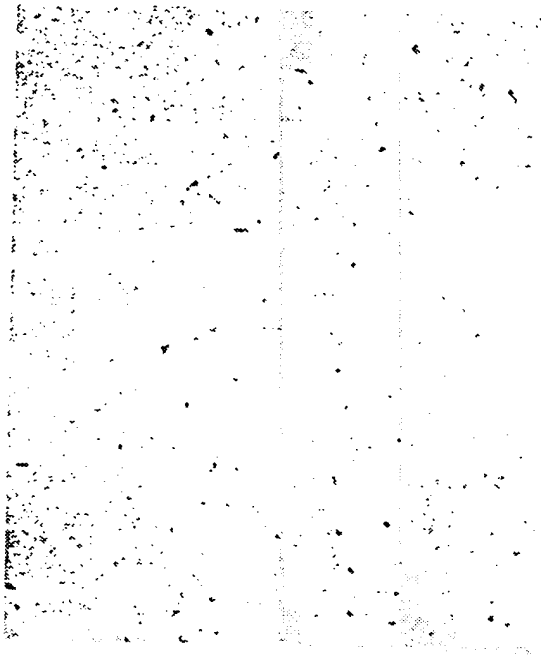

Fig. 3

Fig. 1

Fig. 5

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08J9/18 C08[illegible]8/00 B01J20/22 B01J39/[illegible] //(C08J9/18, C08L25:04),(C08[illegible]/00,212:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 263 407 (REED, JR) 21 April 1981 see column 2, line 54 - column 3, line 12 see column 3, line 39 - column 3, line 63 see column 4, line 33 - column 4, line 64 see claims 1-25 -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
9 November 1993	14. 12. 93

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	OUDOT, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. ional Application No
PCT/US 93/08031

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4263407	21-04-81	CA-A-	1130500	24-08-82
		EP-A,B	0007792	06-02-80
		JP-C-	1477939	27-01-89
		JP-A-	55018297	08-02-80
		JP-B-	62016136	10-04-87